Supporting Information for

Divergent Drivers of Aerosol Acidity: Evidence for Shifting Regulatory Regimes in a Coastal Region

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Text S1. Multiphase buffer theory derivation. In aerosol systems, buffering capacity arises not only from classical acid-base dissociation in the aqueous phase but also from gas-liquid partitioning of volatile conjugate pairs (e.g., NH_4^+/NH_3, HNO_3/NO_3^-). The redistribution of the neutral form between gas and liquid phases introduces additional pathways to mitigate pH perturbations compared to bulk aqueous solutions (Zheng et al., 2020;Gao et al., 2025).

For a volatile weak base (BOH) and its conjugate cation (B^+), the equilibria are:

Gas-liquid partitioning:

$$[\mathrm{BOH(g)}] = K_\mathrm{g} \cdot [\mathrm{BOH(aq)}] \tag{1}$$

$$K_\mathrm{g} = \frac{\rho_\mathrm{w}}{H_\mathrm{BOH} \cdot R \cdot T \cdot \mathrm{AWC}} \tag{2}$$

Acid-base dissociation:

$$[\mathrm{BOH(aq)}] = K_\mathrm{a,BOH} \cdot \frac{[\mathrm{B^+}]}{[\mathrm{H^+}]} \tag{3}$$

Mass balance:

$$[\mathrm{BOH}]_\mathrm{tot}{}^* = [\mathrm{B^+}] + [\mathrm{BOH(aq)}] + [\mathrm{BOH(g)}] \tag{4}$$

where $[\mathrm{BOH(g)}]$ denotes the equivalent molality, defined as the number of moles of gaseous BOH normalized by the mass of aerosol water. K_g is the dimensionless gas-liquid partitioning constant, H_BOH is the Henry's law constant of BOH (mol kg^{-1} atm^{-1}), and $K_\mathrm{a,BOH}$ is its aqueous-phase acid dissociation constant. $[\mathrm{BOH}]_\mathrm{tot}{}^*$ represents the total equivalent molality of BOH (mol kg^{-1}), including aqueous B^+ as well as BOH present in both liquid and gas phases.

These relations lead to an effective dissociation constant that incorporates gas-liquid coupling:

$$K_\mathrm{a,BOH}{}^* = K_\mathrm{a,BOH} \cdot (1 + K_\mathrm{g}) \tag{5}$$

$$K_\mathrm{a,HA}{}^* = \frac{K_\mathrm{a,HA}}{1+K_\mathrm{g}} \tag{6}$$

where $K_{\mathrm{a,HA}}$ is the acid dissociation constant of HA in aqueous solutions.

The ionic concentration can be written as:

$$[\mathrm{B}^+] = \frac{[\mathrm{H}^+]\cdot[\mathrm{BOH}]_{\mathrm{tot}}{}^*}{[\mathrm{H}^+]+K_{\mathrm{a,BOH}}{}^*} \tag{7}$$

When a strong base is added (n_{base}, mol kg^{-1}), the liquid-phase charge balance is:

$$\mathrm{n}_{\mathrm{base}} + [\mathrm{H}^+] + [\mathrm{B}^+] = [\mathrm{OH}^-] + [\mathrm{As}^-] = \frac{K_{\mathrm{w}}}{[\mathrm{H}^+]} + [\mathrm{As}^-] \tag{8}$$

where K_{w} is the water dissociation constant and $[\mathrm{As}^-]$ represents counter-anions from the accompanying salt.

Substituting Eq. (7) yields:

$$\mathrm{n}_{\mathrm{base}} = \frac{K_{\mathrm{w}}}{[\mathrm{H}^+]} - [\mathrm{H}^+] - \frac{[\mathrm{H}^+]\cdot[\mathrm{BOH}]_{\mathrm{tot}}{}^*}{[\mathrm{H}^+]+K_{\mathrm{a,BOH}}{}^*} + [\mathrm{As}^-] \tag{9}$$

The buffering capacity is defined as:

$$\beta = \frac{d\mathrm{n}_{\mathrm{base}}}{d\mathrm{pH}} \tag{10}$$

Differentiating Eq. (9) with respect to $[\mathrm{H}^+]$ and applying $\frac{d[\mathrm{H}^+]}{d\mathrm{pH}} = -2.303[\mathrm{H}^+]$ gives:

$$\beta = 2.303\left(\frac{K_{\mathrm{w}}}{[\mathrm{H}^+]} + [\mathrm{H}^+] + \frac{[\mathrm{H}^+]\cdot K_{\mathrm{a,BOH}}{}^*}{([\mathrm{H}^+]+K_{\mathrm{a,BOH}}{}^*)^2}\cdot[\mathrm{BOH}]_{\mathrm{tot}}{}^*\right) \tag{11}$$

The first two terms correspond to the intrinsic self-buffering of water under strongly acidic or alkaline conditions, while the third term reflects the contribution of the volatile buffer pair, maximized when $[\mathrm{H}^+] \approx K_{\mathrm{a,BOH}}{}^*$.

For a system containing multiple volatile and non-volatile acid-base pairs, the total buffering capacity is additive:

$$\beta = 2.303\left(\frac{K_{\mathrm{w}}}{[\mathrm{H}^+]} + [\mathrm{H}^+] + \sum_k \frac{[\mathrm{H}^+]\cdot K_{\mathrm{a},k}{}^*}{([\mathrm{H}^+]+K_{\mathrm{a},k}{}^*)^2}\cdot[X_k]_{\mathrm{tot}}{}^*\right) \tag{12}$$

where X_k denotes the reservoir of species *k* (gas + aqueous neutral + ionized), and $K_{\mathrm{a},k}{}^*$ is its effective dissociation constant. This formulation shows that each buffer contributes maximally near $\mathrm{pH} \approx \mathrm{p}K_{\mathrm{a},k}{}^{*}$, with the height of the peak proportional to the species abundance.

At high ionic strength, activity coefficients modify the effective dissociation constants. The non-ideal form is written as:

$$K_{\mathrm{a},k}{}^{*,\mathrm{ni}} = K_{\mathrm{a},k}{}^{*} \cdot \frac{\gamma_{\mathrm{H}^{+}} \cdot \gamma X_{k,\mathrm{tot}}}{\gamma_{\mathrm{ion},k}} \tag{13}$$

and Eq. (12) is updated by substituting $K_{\mathrm{a},k}{}^{*}$ with $K_{\mathrm{a},k}{}^{*,\mathrm{ni}}$. For volatile bases such as NH_4^+/NH_3, the gas phase can be treated as ideal ($\gamma \approx 1$), so deviations mainly arise from the ratio $\gamma_{\mathrm{H}^{+}}/\gamma_{\mathrm{ion}}$.

Text S2. Aerosol pH variation drivers. In this study, the changes in aerosol pH (ΔpH) induced by an individual driver were defined as the differences between typhoon and non-typhoon scenarios used as constraints. The constraint ranges were selected to represent the variability observed during the campaign, thereby ensuring that the perturbations remained within realistic atmospheric conditions. The drivers considered included nonvolatile cations (NVCs), total ammonia (TNH_3), total nitric acid ($THNO_3$), relative humidity (RH), and temperature (T).

Aerosol pH was determined using the ISORROPIA II (http://isorropia.epfl.ch) model based on datasets from both typhoon and non-typhoon conditions. Taking the typhoon case as an example, the model was constrained by the chemical and meteorological parameters specific to the typhoon period, while the driver of interest was varied between the typhoon and non-typhoon datasets. The difference between the two simulated pH values was then attributed to the ΔpH caused by that driver under typhoon conditions.

Each driver was evaluated over distinct fixed ranges along the x-axis in Figure 3. Specifically, for chemical composition, we followed the analytical approach of previous study (Zheng et al., 2020), in which the composition profile is normalized by the total equivalent anions. The major influencing factors in the chemical profiles are total HNO_3, non-volatile cations (NVCs), and total NH_3. The difference in our study is that aerosol water content (AWC) was not treated as an independent driver in this part. Instead, all drivers, whether chemical or meteorological, may lead to changes in AWC. Nevertheless, we adopted Zheng et al.'s method for evaluating the chemical drivers to facilitate subsequent comparison of results.

For meteorological factors (RH and T), ΔpH was similarly calculated using the ISORROPIA model by constraining the simulations with typhoon and non-typhoon datasets. Accordingly, the ΔpH contributions of different drivers within the same scenario are not strictly comparable, as the constraint criteria for ΔpH differ among drivers; that is, each driver was assessed over distinct fixed ranges on the x-axis. However, the ΔpH contributions of a given driver between typhoon and non-typhoon scenarios were derived under the same constraint framework and can therefore be meaningfully compared.

Table S1. Equilibrium constants on a molality basis for calculating aerosol buffering capacity.

Gas-aqueous equilibrium

Equilibrium	Constant definition	Constant value (mol kg^{-1} atm^{-1})^{a}			Ref.
		$K\ (T_0)$	$-\frac{\Delta H_{298}}{R \cdot T_0}$	$-\Delta C_{p0}/R$	
$NH_3(g) \leftrightarrow NH_3(aq)$	$H_{NH_3} = \frac{\gamma_{NH_3(aq)} \cdot [NH_3(aq)]}{p_{NH_3}}$	57.64	13.79	-5.39	(Kim et al., 1993)
$HNO_3(g) \leftrightarrow HNO_3(aq)$	$H_{HNO_3} = \frac{\gamma_{HNO_3(aq)} \cdot [HNO_3(aq)]}{p_{HNO_3}}$	2.1×10^{5}	n/a^{b}	n/a	(Kim et al., 1993)

Aqueous ionization equilibrium

Equilibrium	Constant definition	Constant value (mol^{2} kg^{-2} for K_w, mol kg^{-1} for all others)			Ref.
		$K\ (T_0)$	$-\frac{\Delta H_{298}}{R \cdot T_0}$	$-\Delta C_{p0}/R$	
$H_2O \leftrightarrow H^+ + OH^-$	$K_w = \frac{[H^+] \cdot [OH^-] \cdot \gamma_{H^+} \cdot \gamma_{OH^-}}{a_w}$	1.01×10^{-14}	-22.52	26.92	(Kim et al., 1993)
$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$	$K_{b,NH_3} = \frac{[NH_4^+] \cdot [OH^-] \cdot \gamma_{NH_4^+} \cdot \gamma_{OH^-}}{[NH_3] \cdot \gamma_{NH_3} \cdot a_w}$ $K_{a,NH_3} = \frac{K_w}{K_{b,NH_3}}$	1.81×10^{-5}	-1.5	26.92	(Kim et al., 1993)
$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$	$K_{a,HSO_4} = \frac{[H^+] \cdot [SO_4^{2-}] \cdot \gamma_{H^+} \cdot \gamma_{SO_4^{2-}}}{[HSO_4^-] \cdot \gamma_{HSO_4^-}}$	1.02×10^{-2}	8.85	25.14	(Seinfeld and Pandis, 2006)
$HNO_3 \leftrightarrow H^+ + NO_3^-$	$K_{a,HNO_3} = \frac{[H^+] \cdot [NO_3^-] \cdot \gamma_{H^+} \cdot \gamma_{NO_3^-}}{[HNO_3] \cdot \gamma_{HNO_3}}$	15.4	29.17	16.83	(Haynes, 2014)

[a] The equilibrium constant at a specific temperature *T* is:

$$K(T) = K(T_0) \cdot \exp\left[-\frac{\Delta H_{298}}{R \cdot T_0} \cdot \left(\frac{T_0}{T} - 1\right) - \frac{\Delta C_{p0}}{R} \cdot \left(1 + \ln\left(\frac{T_0}{T}\right) - \frac{T_0}{T}\right)\right]$$

, where T_0 = 298.15 K.

[b] Not found and are set to zero.

Table S2. Configuration of typhoon and non-typhoon scenarios in this study[a].

Scenario	Na^+	SO_4^{2-}	TNH_3	$THNO_3$	THCl	Ca^{2+}	K^+	Mg^{2+}	RH	T
Typhoon	0.22	0.54	0.86	0.41	1.84	0.05	0.02	0.04	0.92	298.72
Non-typhoon	0.07	6.13	4.37	1.82	0.46	0.04	0.06	0.01	0.70	301.74

[a] All aerosol compositions are reported in units of μg m^{-3}, relative humidity (RH) is represented on a 0–1 scale, and temperature (T) is given in Kelvin (K).

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